

Nanostructured catalysts for oxygen electroreduction based on bimetallic monoethanolamine complexes of Co(III) and Ni(II)

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Abstract Oxygen reduction electrocatalysts based on the monoethanolmine complexes $\{[\text{CoEtM}]_2(\mu\text{-EtM})_4\text{Ni}(\text{NO}_3)_2\}$ and $\{[\text{CoEtM}]_2(\mu\text{-EtM})_4\text{Ni}(\text{NO}_3)_2\} + \text{activated carbon AG-3}$ have been obtained by high-temperature synthesis. The nature of active centers on the synthesized electrocatalysts was described. Using potentiostatic and cyclic potentiodynamic voltammetry, the kinetic characteristics of catalysts in the oxygen electroreduction reaction were determined. Thermal decomposition of the thermally unstable complexes was described and character of the active centers formed was discussed. The optimal synthesis temperature of electrocatalysts is 600 °C in an inert atmosphere. The calculated exchange current densities for the oxygen electroreduction reaction at the catalysts in 1 M KOH at 20 °C was $j_0 = 1.01 \times 10^{-3} \text{ A g}^{-1}$ – $3.3 \times 10^{-3} \text{ A g}^{-1}$. The Tafel slopes of stationary polarization curves are 0.054–0.063 V for b_1 and 0.106–0.125 V for b_2 . The prepared electrocatalysts can be recommended only for electrochemical systems with alkaline electrolyte.

Keywords Electrochemistry · Oxygen electroreduction · Electrocatalysts · Monoethanolamine complexes · Nanostructure

1 Introduction

The potential of fuel cells to be utilized as clean and efficient power sources for electric vehicles has long been suggested due to their environmental friendliness, low operating temperature and high-energy efficiency characteristics. However, the use of expensive platinum metals as electrocatalysts limits the large-scale production of fuel cells [1–3].

Oxygen or nitrogen containing complexes of 3-d metals [4–6] are interesting as precursors for highly effective oxygen reduction electrocatalysts in chemical fuel cells [7] or sensors. Pyrolysis of oxygen based complexes on a carbon based support can result in formation of catalytically active centers formed by metals, binary oxides or complex oxides like spinels or perovskites. Despite the fact that one of the best oxide-based catalysts is an oxide of 3d metals with a spinel structure [8–11], these materials have a lower electrical conductivity than catalytically active metals or carbon materials. Thus, modification of carbon based supports with these oxides is fairly complicated. It is also well known that electrocatalytical activity of oxides is mostly determined by nature of the cation and presence of structure defects [12, 13].

Heteropolynuclear metal–organic complexes with d-metals contain always metallic atoms bound to ligand through oxygen or nitrogen atoms. Such ordering favors formation of nanostructures containing d-metals bound to carbon surface through nitrogen or oxygen atoms which are electroactive in reactions of oxygen reduction. Amino

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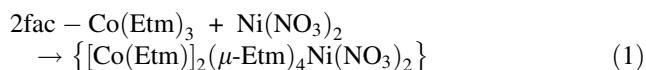
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alcohols are polyfunctional O,N-ligands which are able to attach metal ions as neutral molecules or, in deprotonated form, as aminoalcoholates. It was demonstrated that ions of different metals can form bridge bonds through oxygen atoms forming heterometallic complexes with aminoalcoholates involving various metal ions [14–16].

In this study we use heteropolynuclear complexes synthesized in reaction of $\text{Ni}(\text{NO}_3)_2$ with complex $\text{fac-Co}(\text{Etm})_3$ (Etm = deprotonated monoethanolamine $\text{H}_2\text{NCH}_2\text{CH}_2\text{O}^-$).

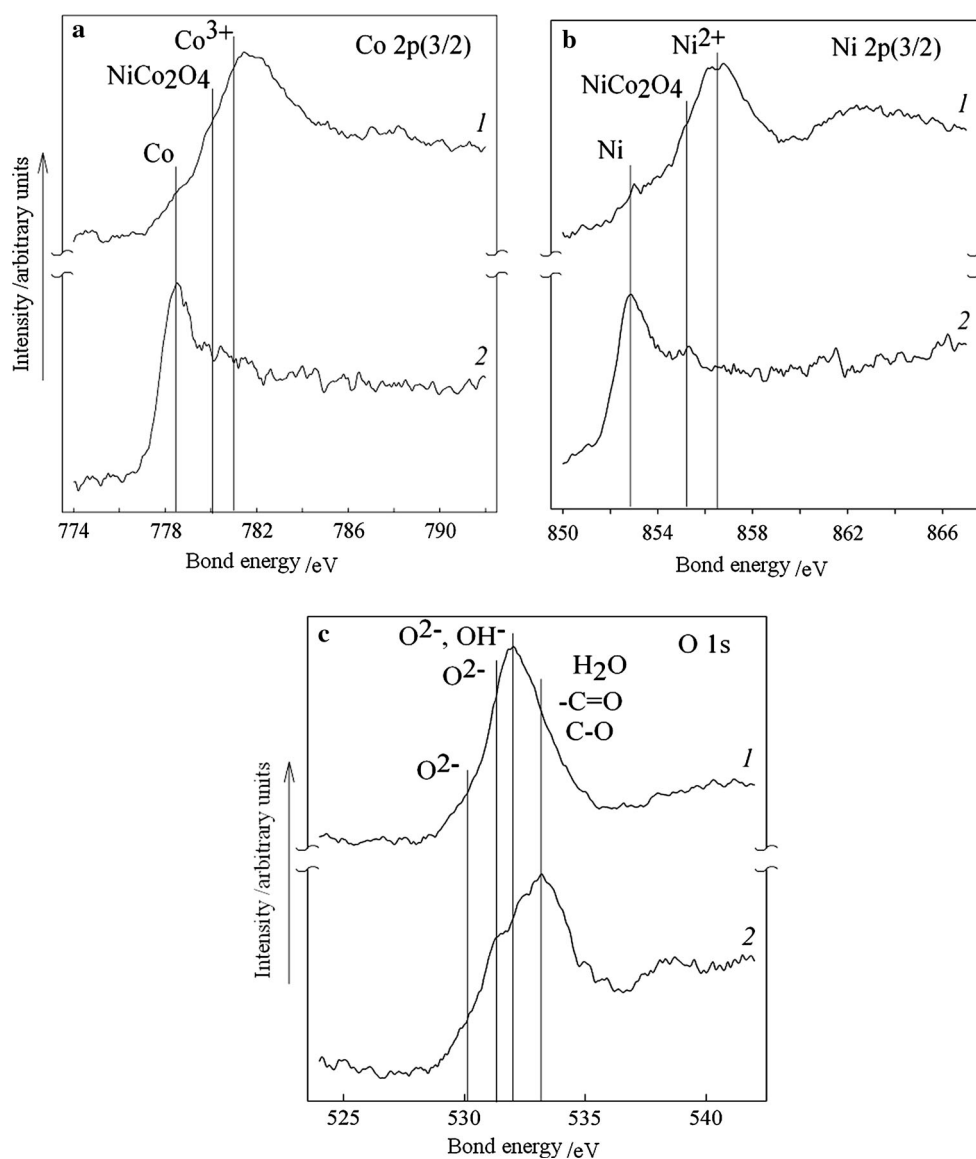
We prepared heteropolynuclear metal–organic complexes with molar ratio of $\text{Co}^{3+}:\text{Ni}^{2+} = 2:1$ according to the reaction 1;



the structure of the compound formed is based on the X-ray derived structure (A) of the initial $\text{fac-Co}(\text{Etm})_3$ complex [17] in which the curves substitutes C_2H_4 , $\text{L} = \text{NO}_3^-$, H_2O or dimethylformamide.

It is well known [18] that thermal destruction of such complexes in carbon matrix begins with splitting of the terminal groups of ligands, residual fragments of complexes come into the structure of carbon matrix. Therefore, we can suppose that during pyrolysis the metal fragments with oxygen in certain temperature interval solidify on the carbon matrix surface as metals, spinels or nonstoichiometric oxides depending on the ratio of metal ions in the initial complex. In the presented paper we studied preparation of electrocatalysts of oxygen reduction containing active centers with metallic or spinel structure by pyrolysis

Fig. 1 XPS spectra of electrocatalyst samples based on Ni–Co complexes with monoethanolamine prepared at 600 °C in Ar. **a** $\text{Co}2\text{p}_{3/2}$ spectra, **b** $\text{Ni}2\text{p}_{3/2}$ spectra, **c** $\text{O}1\text{s}$ spectra



of heterometallic monoethanolamine complexes deposited on carbon matrix surface as well as description of structure and electrochemical properties in reactions of oxygen reduction.

2 Experimental

The fac-Co(Etm)₃ complex was prepared according to a previously published procedure [19]. CoCl₂·6H₂O was dissolved in a minimal amount of methanol, and the solution was replenished with monoethanolamine at a molar ratio of 1:5. The hot solution that formed was cooled, and a concentrated solution of KOH was added at a molar ratio of 1:2.5. The pasty product was allowed to crystallize for 3 days under occasional agitation followed by treatment with methanol and filtration. The residual solid material was washed again with methanol to ensure full removal of the complex. The methanol solution was diluted with 50 mL of ethanol and allowed to crystallize. After

2 days, the crystals were filtered and washed with ethanol. The as-prepared dark blue-violet crystals were dissolved in a minimal amount of water and alkalized slightly with KOH. The solution was filtered and allowed to crystallize in a desiccator filled with dry CaCl₂. The as-obtained crystals were sucked off, washed with ethanol and diethyl ether, and allowed to dry freely on air. The purity of the prepared compound was verified by chemical analysis. In general, the yield was approximately 40 %.

Preparation of electrocatalysts: 1 g of granulated activated carbon AG-3 (SORBENT® Russia, Perm. GOST 20464-75) (particle size <50 μm; BET surface area 850 m² g⁻¹) was mixed with 5 mL of a solution containing fac-Co(Etm)₃ and Ni(NO₃)₂ in dimethylformamide in an amount corresponding to a 10 %wt. content of Co in the carbon support. The Co³⁺:Ni²⁺ ratio was adjusted to 2:1, and the solution was stored for 24 h for adsorption followed by drying until a constant temperature of by 20 °C was achieved. The composition of the solution of the initial complexes in dimethylformamide prior to adsorption on

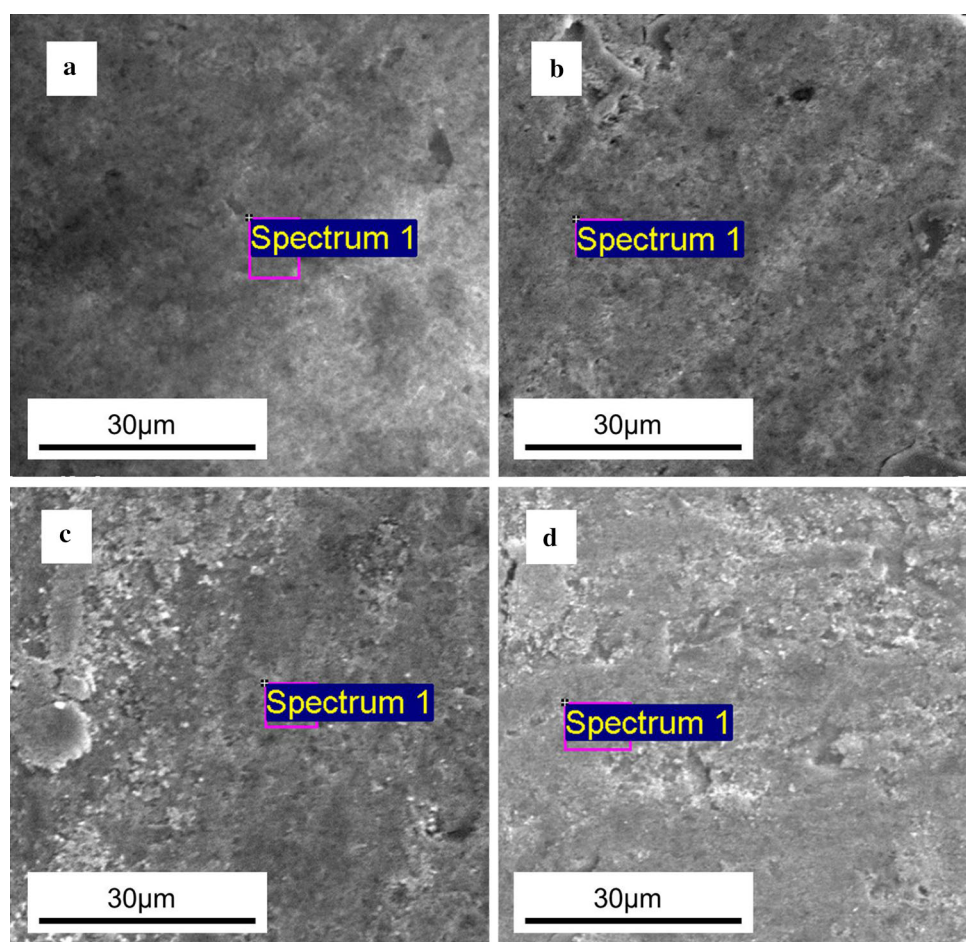


Fig. 2 SEM micrographs of surface of electrocatalysts prepared from {[Co(Etm)₂(μ-Etm)₄Ni(NO₃)₂} at various temperatures. **a** 200 °C, **b** 400 °C, **c** 600 °C, **d** 800 °C

the carbon support was determined using mass spectroscopy AUTOFLEX II (Bruker Daltonics GmbH). Catalytic activity was compared with analogical materials synthesized using the same procedure from aqueous solutions of nitrates of Ni^{2+} and Co^{3+} , ratio of Ni^{2+} : Co^{3+} was 1:1. The salts were deposited on the carbon support in amount corresponding to 10 wt.% of Co. The material was dried at room temperature for 24 h and subsequently pyrolyzed.

200 mg of the dried carbon coated with the precursors was placed into quartz tube furnace in argon atmosphere under continuous flow of gas. The material was then heated to desired temperature and maintained at this temperature for 1 h. The thermal treatment has been carried out at temperatures 200, 400, 600 and 800 °C. Qualitative analysis of the pyrolysis products has been carried out by thermal desorption spectroscopy method [20] using mass spectrometric analysis of the desorbed compounds with MX-1,302 M spectrometer (produced JSC “SELM”, Sumy, Ukraine) at heating rate 10 °C/min and pressure 10^{-6} Pa. The quantity of the tested material was 1 mg.

Electrochemical measurements were carried out using the “floating” gas diffusion electrode [21] in electrochemical cell with separated cathode and anode spaces at

20 °C in 1 mol/L KOH solution using potentiostat PI-50-1.1 (Gomel Plant of Measuring Devices, Gomel, Republic of Belarus) and digital multimeter with USB-interface AXIOMET AX-18B. AgCl electrode has been used as reference.

The “floating” gas diffusion electrode was realized as 10 mm diameter cylindrical flat tablet 2 mm thick, density 0.95 g.cm^{-3} made from carbon black hydrophobized with 30 % polytetrafluoroethylene compressed at 5–7 MPa in which a Ni wire was pressed as current collector. To prepare the electrode, carbon black P-803 (Russian standard GOST 7885-86) was used. The carbon black was hydrophobized with water emulsion of polytetrafluoroethylene FP-4D (Russian standard TU 6-05-12-46-76). A 20 μm thick monolayer of particles of the tested electrocatalyst was placed on surface of the electrode in amount not exceeding 1 mg cm^{-2} and pressed at 5–6 MPa. Monolayer coating of the “floating” gas diffusion electrode ensured equal supply of oxygen to the outer surface of grains of the catalyst.

SEM micrographs and qualitative analysis were made with Scanning Electron Microscope TESCAN VEGA. High resolution TEM micrographs were obtained with the

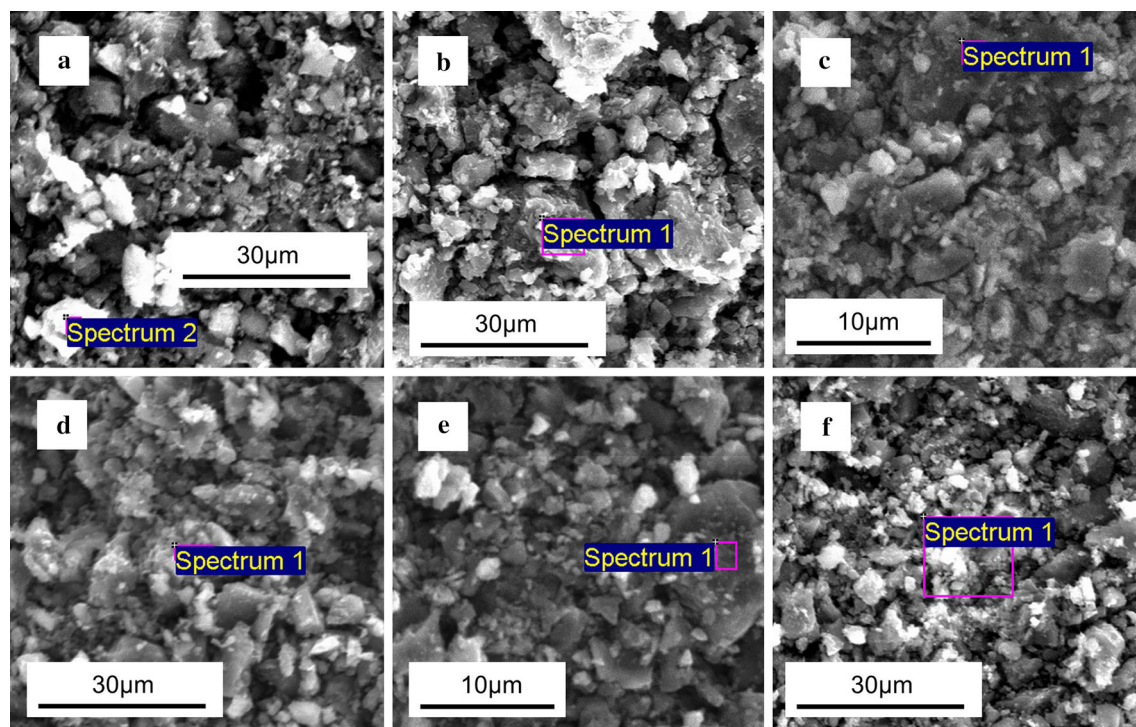


Fig. 3 SEM micrographs showing morphology changes of electrocatalysts prepared at various annealing temperatures of $\{[\text{CoEtM}]_2(\mu\text{-Etm})_4\text{Ni}(\text{NO}_3)_2\}$ deposited on carbon support AG-3. **a** pure AG-3,

b $\{[\text{CoEtM}]_2(\mu\text{-Etm})_4\text{Ni}(\text{NO}_3)_2\}$ deposited on carbon support AG-3 without thermal treatment, **c** annealed at 200 °C, **d** annealed at 400 °C, **e** annealed at 600 °C, **f** annealed at 800 °C

300 kV Transmission Electron Microscope JEOL JEM 3010 equipped with EDS detector Oxford Instruments.

IR spectra ($400\text{--}4,000\text{ cm}^{-1}$) were obtained with the spectrophotometer Specord-M80. The IR spectra of powders were measured in KBr pellets.

Phase composition of electrocatalysts was determined with powder X-ray diffractometer DRON-3 M using radiation of the $\text{CuK}\alpha_1$ line (wavelength $1.54\text{ }10^{-10}\text{ m}$) and Ni filter. The respective phases were identified using the ASTM database.

Electron structure of electrocatalysts surfaces was determined using the X-ray photoelectron spectroscopy with the EC-2402 spectrometer equipped with PHOIBOS-100_SPECS energy analyzer (E $\text{MgK}\alpha = 1,253.6\text{ eV}$, $\Delta E_{1/2} = 0.680\text{ eV}$, $P_{\text{max}} = 300\text{ W}$). Working pressure in the spectrometer chamber was $\sim 2 \times 10^{-5}\text{ Pa}$. Absolute discrimination determined using the $\text{Au}4f_{7/2}$ peak was 0.85 eV at signal intensity $30,000\text{ imp.s}^{-1}$. The accuracy of determination of peak position was better than 0.05 eV . Spectrometer calibration was carried out at the onset,

middle and end of the energy scale using peaks of $\text{Cu}2p_{3/2}$ -, $\text{Cu}3p$ -, $\text{Au}4f_{7/2}$ -, and $\text{Au}4d_{5/2}$ -lines. The samples were deposited on surface of $10 \times 10\text{ mm}$ Al plates.

3 Results and discussion

Active centers on surface of electrocatalysts were studied on heteropolynuclear Co–Ni complex with monoethanolamine with ratio of $\text{Co}^{3+}:\text{Ni}^{2+}=2:1$ synthesized according to the Eq. 1. To characterize the thermolysis products we studied thermal analysis of the $\{[\text{CoEtM}]_2(\mu\text{-EtM})_4\text{Ni}(\text{NO}_3)_2\}$ complex. We observed that above $105\text{ }^\circ\text{C}$ complex decomposes in a three stage process. The first stage between $105\text{--}205\text{ }^\circ\text{C}$ two nitrate anions are split off, the first before $185\text{ }^\circ\text{C}$ and the second above this temperature; the wt. loss related with this process was 14% . At $205\text{--}240\text{ }^\circ\text{C}$ four monoethanolamine ligands are split off (wt. loss 39.8%), the last stage at $240\text{--}700\text{ }^\circ\text{C}$ the remaining two ethanolamine ligands are released (18.2%).

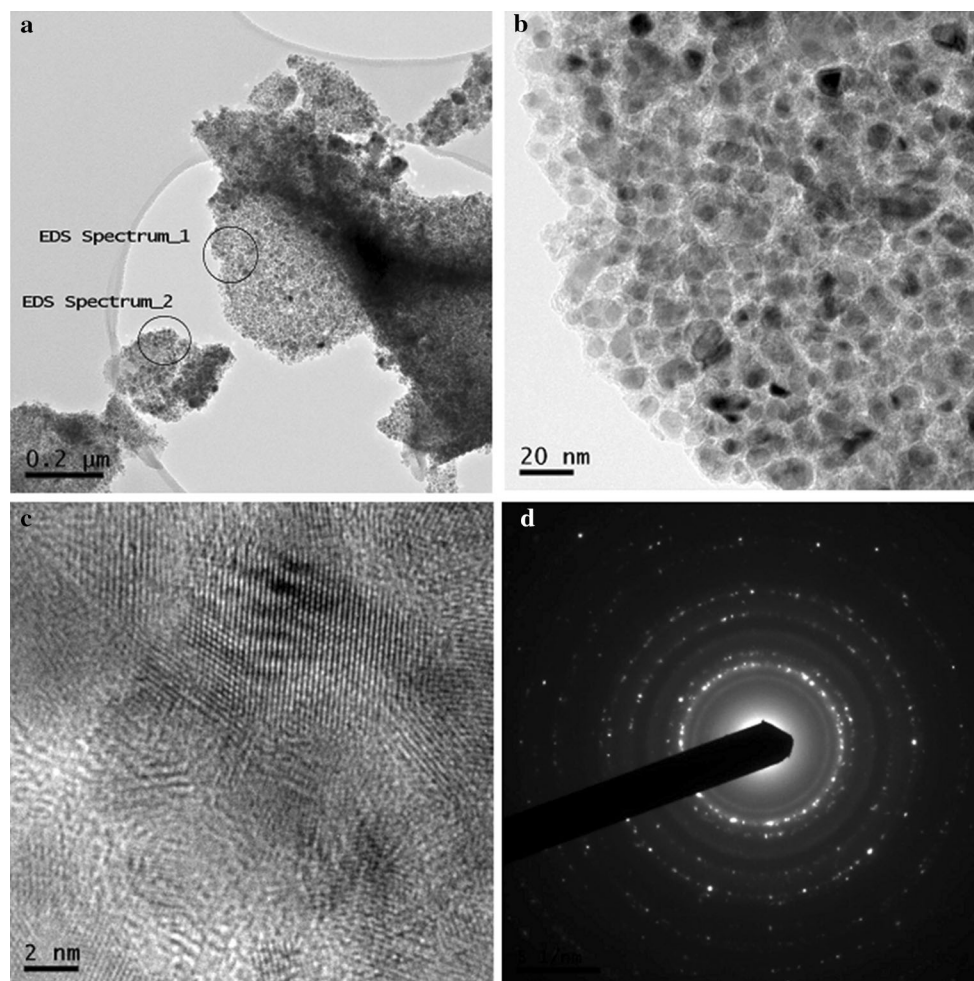


Fig. 4 HRTEM micrographs of products of thermal decomposition of the $\{[\text{CoEtM}]_2(\mu\text{-EtM})_4\text{Ni}(\text{NO}_3)_2\}$ complex at $600\text{ }^\circ\text{C}$ with various magnification (**a–c**) and their electron diffraction pattern (**d**)

Composition of the pyrolysis product corresponds to NiCo_2O_4 (28 % by wt. of the starting material).

Contrary to the decomposition of the pure complex, the three stages decomposition of the composite $\{[\text{CoEtM}]_2(\mu\text{-EtM})_4\text{Ni}(\text{NO}_3)_2\}$ with carbon AG-3 proceeds with simultaneous reduction of metal oxides. During the first stage between 80–140 °C two nitrate anions are split off; the wt. loss related with this process is 4.7 %. At 140–250 °C three monoethanolamine ligands are split off (wt. loss 9.2 %), the last stage at 250–800 °C the remaining two ethanolamine ligands are released (10 %). The composition of the pyrolysis product corresponds to NiCo_2 (9.02 %).

XPS spectra of $\text{Ni}2\text{p}_{3/2^-}$, $\text{Co}2\text{p}_{3/2^-}$, and O1s were measured to characterize the surface properties of electrocatalysts. The curve 1, Fig. 1 A shows spectrum of $\text{Co}2\text{p}_{3/2}$ prepared from the monoethanolamine complex at 600 °C in Ar atmosphere. The bond energy $E_b = 780.9$ eV correspond to Co^{3+} valence. The bond energy $E_b = 780.1$ eV is typical for Ni-Co spinel. The catalyst prepared from composite containing monoethanolamine complex and carbon contains cobalt ions reduced to metallic state and band with typical bond energy $E_b = 778.5$ eV which can be observed in the XPS spectrum (see curve 2 on Fig. 1a). According to this curve small amount of spinel with $E_b = 780.1$ is also present in this sample. Similar picture we can see also on the XPS spectra of Ni atoms present in the catalyst (Fig. 1b, curve 1). The bond energy of Ni $2\text{p}_{3/2}$ $E_b = 856.4$ eV corresponds to Ni^{2+} state. We can observe also line with $E_b = 855.4$ eV typical for Ni-Co spinel structure. In the material deposited on carbon support reduction of Ni^{2+} to metallic state occurs corresponding to line with $E_b = 852.8$ eV (Fig. 1b, curve 2). Also on this curve small amount of Ni-Co spinel is present ($E_b = 855.4$ eV).

The XPS spectrum O 1s shows signals with values of $E_b = 530, 531.5$ and 532 eV which are typical for O^{2-} . Most probably, these oxygen atoms can be ascribed to oxygen atoms bound in Ni-Co spinel. Signal of O 1s at $E_b = 533.2$ eV corresponds to bonds in C–O, –C=O as well as H_2O , whereas the signal at $E_b = 532$ eV corresponds to OH^- ions. From analysis of these data one can conclude that calcination at 600 °C of Ni-Co complex with monoethanolamine and without carbon support leads to formation of active centers NiCo_2O_4 type - active centre of $\text{M}(1)\text{M}(2)_2\text{O}_4$ type. However, catalyst synthesized at these conditions contains also small amounts of organic residua formed during thermal decomposition of monoethanolamine ligand. In contrary, for the complex deposited on carbon support reduction of part of Ni and Co ions to metals and active centers $\text{M}(1) + \text{M}(2) + \text{M}(1)\text{M}(2)_2\text{O}_4$ was observed.

The results show that the ethanolamine complexes do not form during thermal decomposition products similar to the materials formed on carbon support, as can be seen

from comparison of SEM micrographs (Fig. 2) taken on samples prepared from the $\{[\text{CoEtM}]_2(\mu\text{-EtM})_4\text{Ni}(\text{NO}_3)_2\}$ complex annealed without carbonaceous support and of the morphology of products prepared from $\{[\text{CoEtM}]_2(\mu\text{-EtM})_4\text{Ni}(\text{NO}_3)_2\}$ complex deposited on the carbon support (Fig. 3b) and products of its annealing (Fig. 3c–f).

The micrographs show changes of the surface morphology resulting from thermal treatment. At 200 °C (Fig. 3c) the complex starts to decompose. This process is accompanied with slight signs of surface melting. At higher temperatures (i.e., from 400 to 800 °C), the surface of the solid product increases, which is consistent with the complete decomposition of the complex. Thus, the morphology changes indicate that the pure complex provides metal oxide compounds on annealing without formation of coke. The same complex deposited on carbon support provides, except of part of oxides, primarily metals resulting from pyrolysis processes and reactions with carbon.

More detailed features of the electrocatalysts structure were obtained with the aid of high resolution TEM images. Figure 4 shows products of thermal decomposition of the $\{[\text{CoEtM}]_2(\mu\text{-EtM})_4\text{Ni}(\text{NO}_3)_2\}$ complex at 600 °C.

Particles of the electrocatalyst can be shown on the micrographs given on Fig. 4. The material consists of 20–30 nm heterogeneous particles (see Fig. 4a–b) which are composed from randomly oriented nanocrystals ~5 nm in size (see Fig. 4c). Chemical composition of

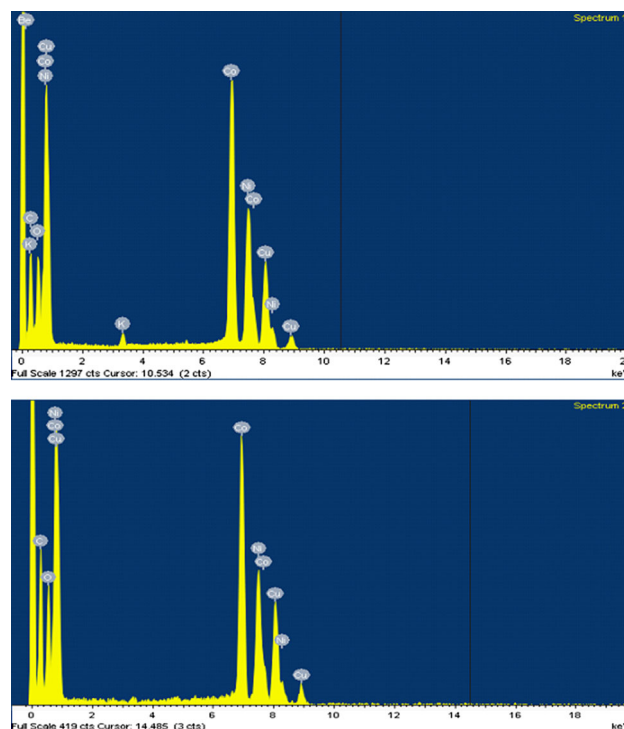


Fig. 5 EDS spectra of the electrocatalyst based on Co–Ni complex with monoethanolamine. Spectra were taken from areas marked on Fig. 4a. **a** EDS spectrum 1, **b** EDS spectrum 2

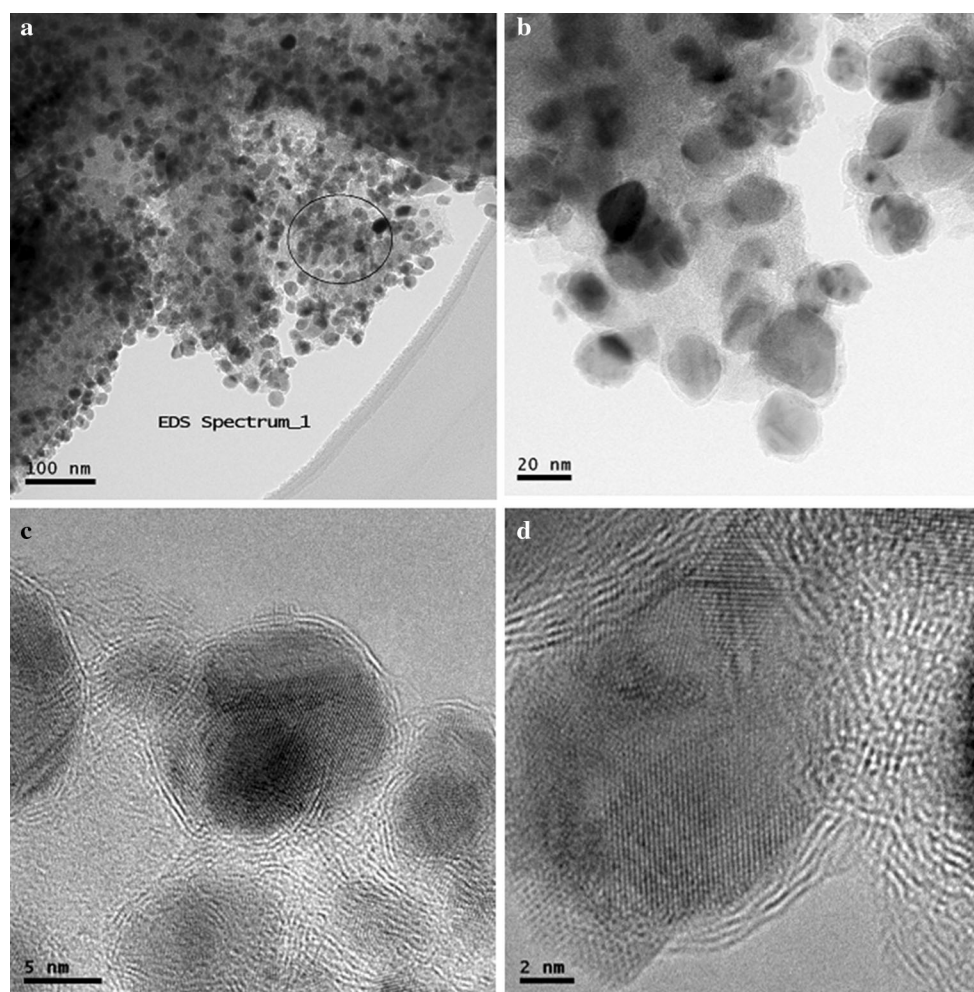


Fig. 6 HRTEM micrographs of products of thermal decomposition of the $\{[\text{CoEtm}]_2(\mu\text{-Etm})_4\text{Ni}(\text{NO}_3)_2\}$ complex deposited on the carbon support AG-3 annealed at 600 °C

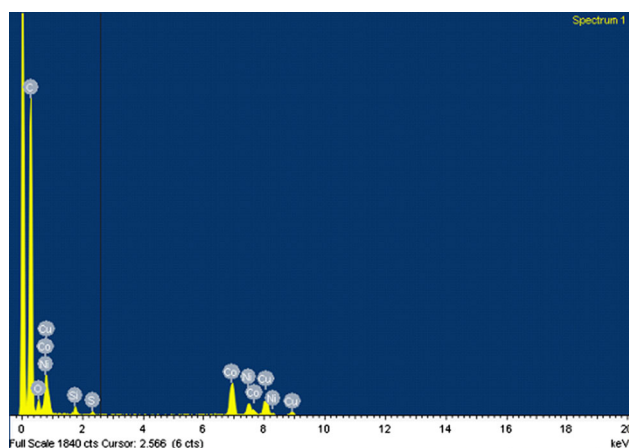


Fig. 7 EDS spectra of the electrocatalyst based on Co–Ni complex with monoethanolamine deposited on carbon support AG-3. Spectra were taken from area marked on Fig. 6a as EDS spectrum 1

particles is presented on Fig. 5. Except of peaks corresponding to Cu and Be resulting from the Cu grid used and Be sample holder, the EDS spectra contain only peaks corresponding to Ni, Co and C. Chemical composition calculated from the EDS spectra corresponds well to compositions expected for spinel type oxides with composition NiCo_2O_4 with carbon admixtures. Very weak K peak visible in both spectra correspond to impurity with concentration in range $\sim 0.4\%$ and lower.

The micrographs presented on the Fig. 6 show particles of the annealing products of the Co–Ni complex deposited on carbon support AG-3. The material consists of ~ 10 nm particles in which dense packed randomly oriented nanocrystals of metal oxide compounds are present (see Fig. 6d). EDS spectrum of this material is presented on Fig. 7 (area denoted on Fig. 6a). Results of the EDS spectrum indicate that on the carbon support are present

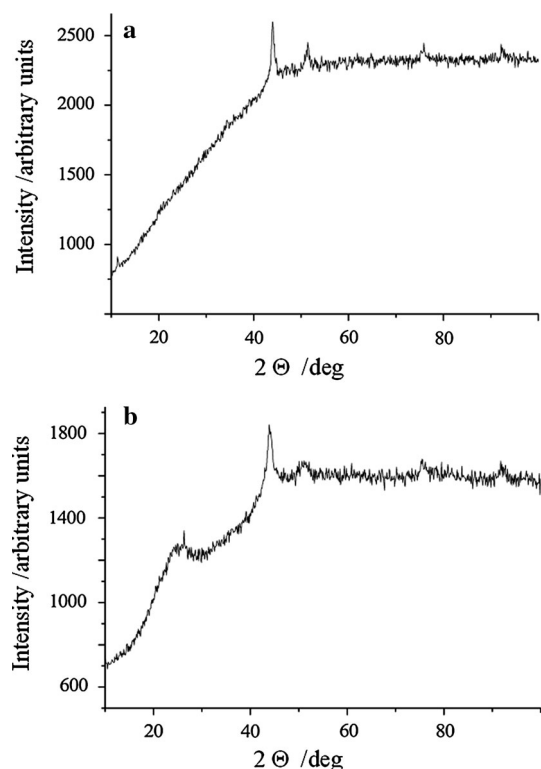


Fig. 8 Powder XRD patterns of electrocatalyst based on Co-Ni complex with monoethanolamine annealed at 600 °C in Ar atmosphere. **a** without carbon support, **b** material deposited on AG-3 carbon support

both Ni-Co oxides (spinel) as well as metals formed on the carbon support by reduction of oxides during pyrolysis. However, the content of C is much higher in comparison to sample prepared without carbon support.

Powder X-ray diffraction patterns of electrocatalysts prepared from $\{[\text{CoEtm}]_2(\mu\text{-Etm})_4\text{Ni}(\text{NO}_3)_2\}$ complexes are presented on Fig. 8, the phases were identified according to ASTM data. As can be concluded from the Fig. 8, the main part of the material consists of phase amorphous to X-rays with inclusions of metal oxides, the crystalline phase form only approx. 3–5 % of the material and, therefore, the phase analysis based on X-ray diffraction analysis is difficult. However, phases of reduced metals Co and Ni can be reliably identified in the diffraction patterns.

Figure 8a shows XRD pattern of material prepared from pure complex $\{[\text{CoEtm}]_2(\mu\text{-Etm})_4\text{Ni}(\text{NO}_3)_2\}$ by annealing at 600 °C. Except of X-ray amorphous main component, nanocrystalline Ni (interplanar distance 2,04; 1,77; 1,25 Å), and Co (interplanar distance 2,05; 1,77; 1,07) phases were detected.

Figure 8b shows XRD pattern of material prepared from complex $\{[\text{CoEtm}]_2(\mu\text{-Etm})_4\text{Ni}(\text{NO}_3)_2\}$ deposited on the carbon support AG-3 by annealing at 600 °C. Except of

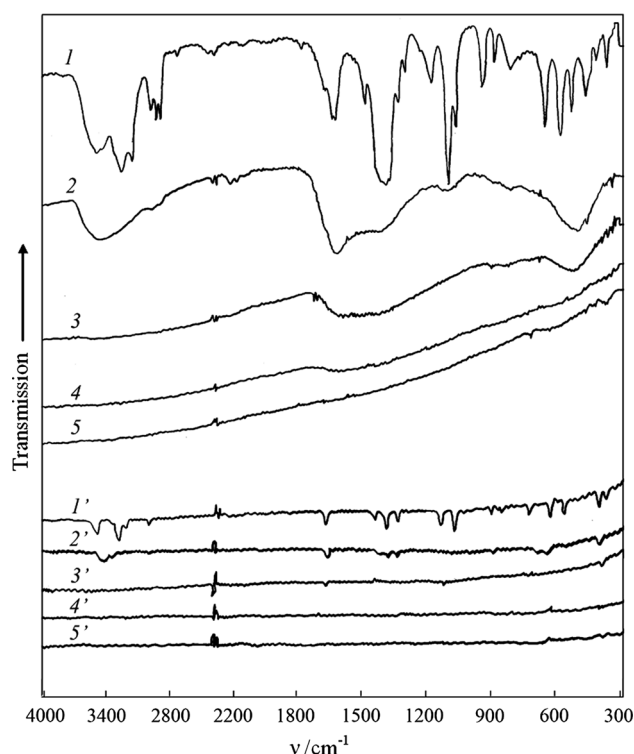


Fig. 9 IR spectra of the $\{[\text{CoEtm}]_2(\mu\text{-Etm})_4\text{Ni}(\text{NO}_3)_2\}$ complex annealed at various temperatures: without support: 1 20 °C, 2 200 °C, 3 400 °C, 4 600 °C, 5 800 °C, deposited on carbon support AG-3: 1' 20 °C, 2' 200 °C, 3' 400 °C, 4' 600 °C, 5' 800 °C

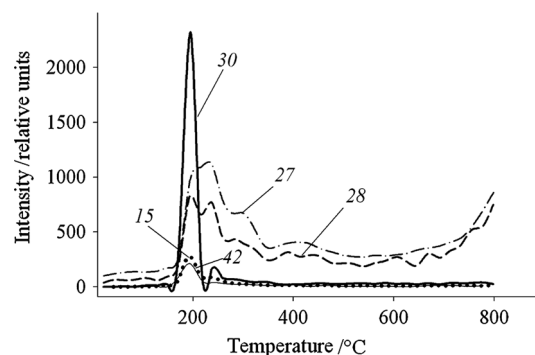


Fig. 10 Thermal desorption curves of the $\{[\text{CoEtm}]_2(\mu\text{-Etm})_4\text{Ni}(\text{NO}_3)_2\}$ complex measured at 10^{-6} Pa and temperature increase rate 10 °C/min. *m/z*: 15 (–NH), 27 ($\text{CH}_2\text{-CH-}$, CH-N- , CH-N- , C-NH-), 28 ($\text{CH}_2\text{-CH}_2\text{-}$, CH-NH- , $\text{CH}_2\text{-N-}$, $\text{C-NH}_2\text{-}$), 30 (–NO)

prevailing part of X-ray amorphous phase partially composed of carbonaceous material, nanocrystalline phases of Ni (2.04; 1.77; 1.25; 1.06 Å), Co (2.05; 1.77; 1.07 Å), NiO (2.09; 1.48 Å) and a phase well corresponding to disordered graphite (3.42 Å) were detected. Metal oxide compounds were not detected in the XRD patterns owing to poor crystallinity.

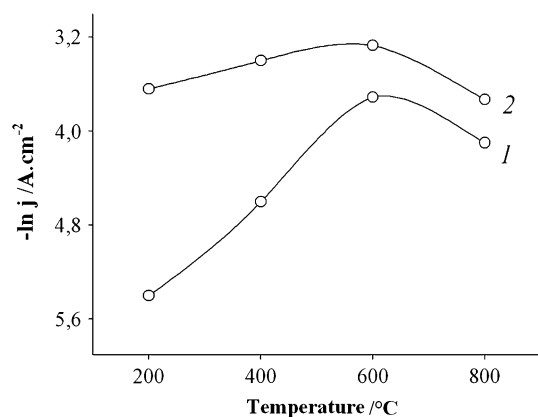


Fig. 11 Dependence of catalytic oxygen electroreduction on catalysts prepared from the $\{[\text{CoEtm}]_2(\mu\text{-Etm})_4\text{Ni}(\text{NO}_3)_2\}$ complex on the annealing temperature. 1 catalyst prepared from the pure complex, 2 catalyst prepared from the complex deposited on carbon support AG-3

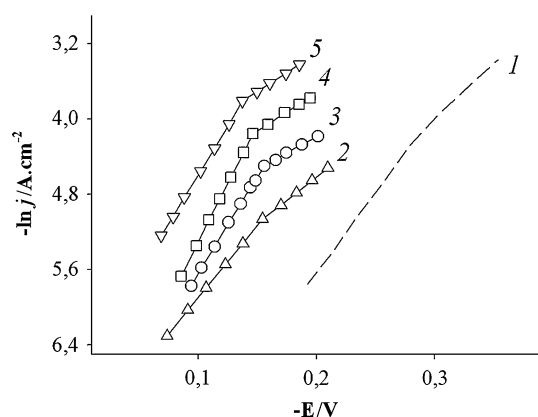


Fig. 12 Stationary polarization curves obtained on catalysts-pyrolysis products of the $\{[\text{CoEtm}]_2(\mu\text{-Etm})_4\text{Ni}(\text{NO}_3)_2\}$ complex: 1 carbon black, 2 200 °C, 3 400 °C, 4 800 °C, 5 600 °C

The IR spectra of annealed material presented on Fig. 9 agree well with data obtained with thermal analysis and scanning electron microscopy. Spectra measured on annealed samples at various temperatures prepared from pure complex $\{[\text{CoEtm}]_2(\mu\text{-Etm})_4\text{Ni}(\text{NO}_3)_2\}$ (curves 1–5) as well as complex deposited on carbon AG-3 (curves 1'–5') shows dynamics of thermal decomposition of the initial material. IR spectra presented in Fig. 9 indicate that the complex $\{[\text{CoEtm}]_2(\mu\text{-Etm})_4\text{Ni}(\text{NO}_3)_2\}$ is quite stable until 200 °C and decomposes gradually between 400 and 600 °C (curves 1–3). Unfortunately, owing to poor transparency of the carbonaceous support, the IR spectra of the complex deposited on the support do not provide information about complex decomposition. The vibration modes are visible only until 200 °C (curves 1'–2'). Based on the analysis of the thermal desorption curves (Fig. 10), the primary component of the gaseous decomposition products is released

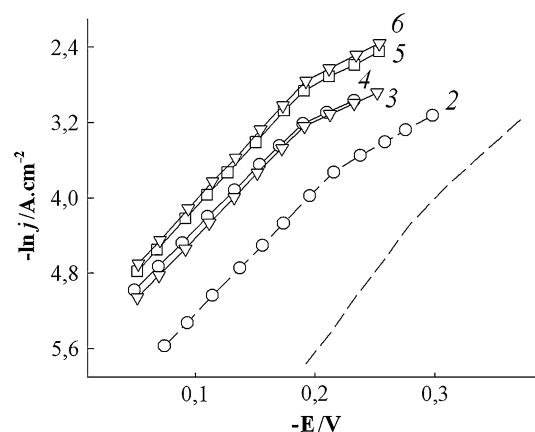


Fig. 13 Stationary polarization curves obtained on catalysts – pyrolysis products of the $\{[\text{CoEtm}]_2(\mu\text{-Etm})_4\text{Ni}(\text{NO}_3)_2\}$ complex + carbon support AG-3: 1 carbon black, 2 pure carbon support AG-3, 3 200 °C, 4 400 °C, 5 800 °C, 6 600 °C

at 200–300 °C. The mass spectra show that in the thermodesorption products there are both nitrate ion fragments as $-\text{NO}$ with $m/z = 30$ and desorbed monoethanolamine particles, $m/z = 15$ ($-\text{NH}$); 27 ($\text{CH}_2\text{-CH-}$, CH-N- , CH-N- , C-NH-); 28 ($\text{CH}_2\text{-CH}_2\text{-}$, CH-NH- , $\text{CH}_2\text{-N-}$, $\text{C-NH}_2\text{-}$), which confirms the DTA data on the beginning and maximum decomposition peak of monoethanolamine.

Figure 11 shows the dependence current density of the catalytic oxygen electroreduction in 1 M KOH at $E = 0.15$ V for catalysts prepared from the $\{[\text{CoEtm}]_2(\mu\text{-Etm})_4\text{Ni}(\text{NO}_3)_2\}$ complex on the annealing temperature. Curve 1 shows the results for the catalyst prepared from the pure complex, and curve 2 shows the activity of the pyrolysis products of the complex deposited on the AG-3 carbon support. Based on the results in Fig. 11, the most active materials were formed at 600 °C. Simultaneously, the material obtained from the complex deposited on the carbon support exhibited a higher activity compared to the decomposition products from the pure complex.

The following parameters were used as criteria of estimation of the activity of electrocatalysts in the oxygen reduction reaction: slope angles of stationary polarization curves, b_1 and b_2 (V); shift of potentiostatic curve to the positive-potential region relative to that for the substrate, ΔE (V); exchange current j_0 (A g^{-1}); activity of electrocatalyst, j (A g^{-1}) at the constant potential E (V).

Figures 12 and 13 show the stationary polarisation dependencies of the current density of oxygen reduction on the polarisation of the electrode. The slopes of the stationary polarisation curves obtained for the studied electrocatalysts are similar to the slopes obtained with carbon based materials. The most active electrocatalysts were prepared from the thermal decomposition of the $\{[\text{CoEtm}]_2(\mu\text{-Etm})_4\text{Ni}(\text{NO}_3)_2\}$ complex deposited on the AG-3

Fig. 14 Cyclic voltammetry curves measured in 1 M KOH at 20 °C and scanning rate 20 mV/s. 1 atmosphere O₂, 2 atmosphere Ar.

a electrocatalysts prepared at 600 °C from {[CoEtm]₂(μ-Etm)₄Ni(NO₃)₂} complex; **b** electrocatalysts prepared at 600 °C from (CoEtm)₂(μ-Etm)₄Ni(NO₃)₂ complex + AG-3

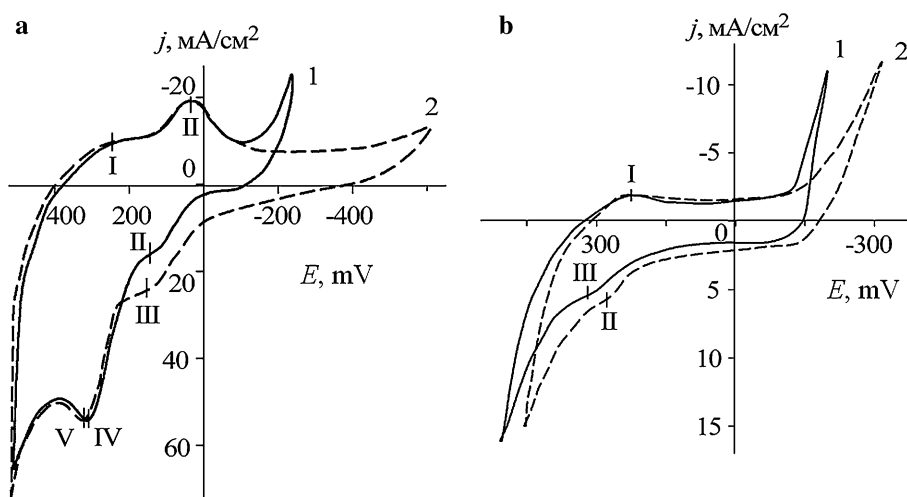


Table 1 Kinetic parameters of electrocatalytic oxygen reduction on catalysts prepared by pyrolysis of {[CoEtm]₂(μ-Etm)₄Ni(NO₃)₂} and {[CoEtm]₂(μ-Etm)₄Ni(NO₃)₂} + AG-3 measured at 20 °C in 1 M KOH

Catalyst	<i>t</i> (°C)	<i>E</i> _{st} (V)	<i>j</i> ₀ (A g ⁻¹)	∂ <i>E</i> /∂lg <i>j</i> (V)	
				<i>b</i> ₁	<i>b</i> ₂
P-803 + 30 %PTFE	20	−0.121	1.00 × 10 ^{−5}	0.065	0.119
AG-3	20	−0.036	2.40 × 10 ^{−4}	0.062	0.121
{[CoEtm] ₂ (μ-Etm) ₄ Ni(NO ₃) ₂ } + AG-3	200	−0.089	1.01 × 10 ^{−3}	0.062	0.118
	400	−0.086	2.60 × 10 ^{−3}	0.056	0.118
	600	−0.076	3.30 × 10 ^{−3}	0.056	0.118
	800	−0.090	1.25 × 10 ^{−3}	0.054	0.106
	200	−0.100	1.29 × 10 ^{−3}	0.068	0.118
{[CoEtm] ₂ (μ-Etm) ₄ Ni(NO ₃) ₂ }	400	−0.083	1.28 × 10 ^{−3}	0.058	0.122
	600	−0.100	4.80 × 10 ^{−3}	0.060	0.120
	800	−0.080	1.35 × 10 ^{−3}	0.062	0.126

t, °C Annealing temperature, *E*_{st} steady-state potential of the gas diffusion electrode, *b*₁ and *b*₂ slopes of the kinetic curves, *j*₀ the current exchange

carbonaceous support at 600 °C. The overvoltage of the oxygen reduction decreased by 0.100 V with this electrocatalyst and by 0.080 V with a similar electrocatalyst prepared without the AG-3 carbon support.

Cyclic voltammetry curves measured in 1 M KOH at 20 °C and scanning rate 20 mV/s in atmosphere of O₂ and Ar are given in Fig. 14. We can conclude that the synthesized electrocatalysts possess highly extended surface which manifests in rising of currents. We observed that the electrocatalyst degrade under effect of positive potential which means that these electrocatalysts can be used effectively only for cathode processes of oxygen reduction. The threshold current values on cyclic voltammetry curves for electrocatalysts based on {[CoEtm]₂(μ-Etm)₄Ni(NO₃)₂} (peaks I–VI) and {[CoEtm]₂(μ-Etm)₄Ni(NO₃)₂} (peaks I–III) correspond to surface reactions of Co and Ni indicating that these metals are charged and are bound in oxide structures.

Kinetic parameters of electrocatalytic oxygen reduction are given in Table 1. Obviously, the highest values of the exchange current densities *j*₀ 1.01 × 10^{−3} A g^{−1}–

3.3 × 10^{−3} A g^{−1} were obtained with the catalysts prepared at the annealing temperature 600 °C. Slopes of he kinetic curves are between 0.054–0.063 V for *b*₁ and 0.106–0.125 V for *b*₂. We can conclude on the basis of kinetic data that the mechanism of oxygen electroreduction proceeds by one electron transfer with retarded addition of the first electron via formation of hydrogen peroxide. A similar mechanism has been proposed for activated charcoal [22] according to the following reaction scheme where M is the active centre on the catalyst:



Then, the reaction continues either by dissociation of the O–O bond or the intermediate formation of hydrogen peroxide. In the low-polarization range, the slowed-down stage may be the attachment of the first electron according to the scheme (3) or (4). These mechanisms are explained by the slopes of lg *j*, *E* curves and the dependence of *E* on

pH. The stationary polarization curves are well described for the low current densities using Eqs. (5).

$$E_1 = \text{const} + \frac{2.3 \times RT}{F} (\lg p_{O_2} - \lg [\text{OH}^-] - \lg j) \quad (5)$$

When the potential shifts to the cathode region, the rate limiting process involves the addition of the first electron resulting in an increase in the slope of $dE/d(\lg j)$ to 100 mV and a decrease in the rate of oxygen electroreduction, which is in agreement with the experimental and calculated data (6)

$$E_2 = \text{const} + \frac{2.3 \times 2RT}{F} \lg p_{O_2} - \frac{2.3 \times RT}{F} \lg [\text{OH}^-] - \frac{2.3 \times 2RT}{F} \lg j \quad (6)$$

4 Conclusions

The studied complexes are characterized by presence of metal atoms bound to ligands through oxygen and nitrogen atoms. Such ordering favors formation of electrocatalytically active centers for electroreduction of oxygen based on d-metals or d-metals attached to carbon surface through oxygen or nitrogen atoms during modification carbonaceous support. Our results indicate that the initial Co–Ni complexes with monoethanolamine $\{[\text{CoEtm}]_2(\mu\text{-Etm})_4\text{Ni}(\text{NO}_3)_2\}$ and $\{[\text{CoEtm}]_2(\mu\text{-Etm})_4\text{Ni}(\text{NO}_3)_2\} + \text{AG-3}$ are thermally unstable and products of their pyrolysis provide active centers $\text{M}(1)\text{M}(2)_\text{M}\text{NO}_\text{Z}$ (without carbon support) or $\text{M}(1)\text{M}(2) + \text{M}(1)\text{M}(2)_\text{M}\text{NO}_\text{Z}$ (complex on carbon support). The optimum pyrolysis temperature was determined to 600 °C.

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